

THE OCCURRENCE OF CHAIN TRANSFER IN THE ANIONIC
POLYMERIZATION OF 9-VINYLANTHRACENE*

In the course of investigating the electrical properties of the vinyl aromatic polymers, repeated attempts were made to prepare high molecular weight poly-9-vinylnanthracene. These efforts were unsuccessful (1) as the maximum number-average degree of polymerization that could be obtained directly was of the order of 10, while fractionation yielded a value of 25. In order to elucidate the reason for the exclusive formation of low molecular weight polymer even when using high M_0/X_0 ratios (where M_0 is the original monomer concentration and X_0 the concentration of "living ends"), it was decided to study the kinetics of the anionic polymerization of this monomer.

In most anionic polymerizations the rates are very rapid and, therefore, special techniques have to be employed (2). In the case of 9-vinylnanthracene, however, the polymerization rate appeared to be sufficiently slow for the application of accurate dilatometric procedures, and this, indeed, was found to be the case. The dilatometric measurements were carried out using the usual high vacuum techniques (3). The solution of the monomer in tetrahydrofuran was titrated with the initiator to a green end point and only the amount added after this titration was used to calculate the concentration of "living ends."

Figure 1 shows representative kinetic results obtained with sodium naphthalene in tetrahydrofuran (THF) at 25°C., where M_0/M_t is plotted on a logarithmic scale against time (M_t is the monomer concentration at time t). The values of M_0/M_t were obtained by the usual method of interpretation of dilatometric rate studies. The additional data for these runs, as well as all the results of the other experiments pertinent to this problem, are recorded in Table I. The number-average degree of polymerization also shown in Table I was determined by means of a Mechrolab osmometer.

The linearity of the plots in Figure 1 proves conclusively that the concentration of "living ends" remains unchanged during the course of polymerization, and the experimentally determined degree of polymerization should have corresponded to the concentration of initiator. As this is not the case, chain transfer is the only reasonable explanation of the low molecular weights observed.

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Several species are present in the solution, i.e., monomer, polymer, initiator, and solvent. The fact that the variation in initiator concentration over more than two orders of magnitude leads to essentially identical molecular weights excludes the possibility of chain transfer to initiator. If chain transfer were to occur predominantly to the polymer, the molecular weights would tend to approach the values predicted from the M_0/X_0 ratios since, under these circumstances, chain transfer to polymer would not lower the average molecular weight significantly. Fur-

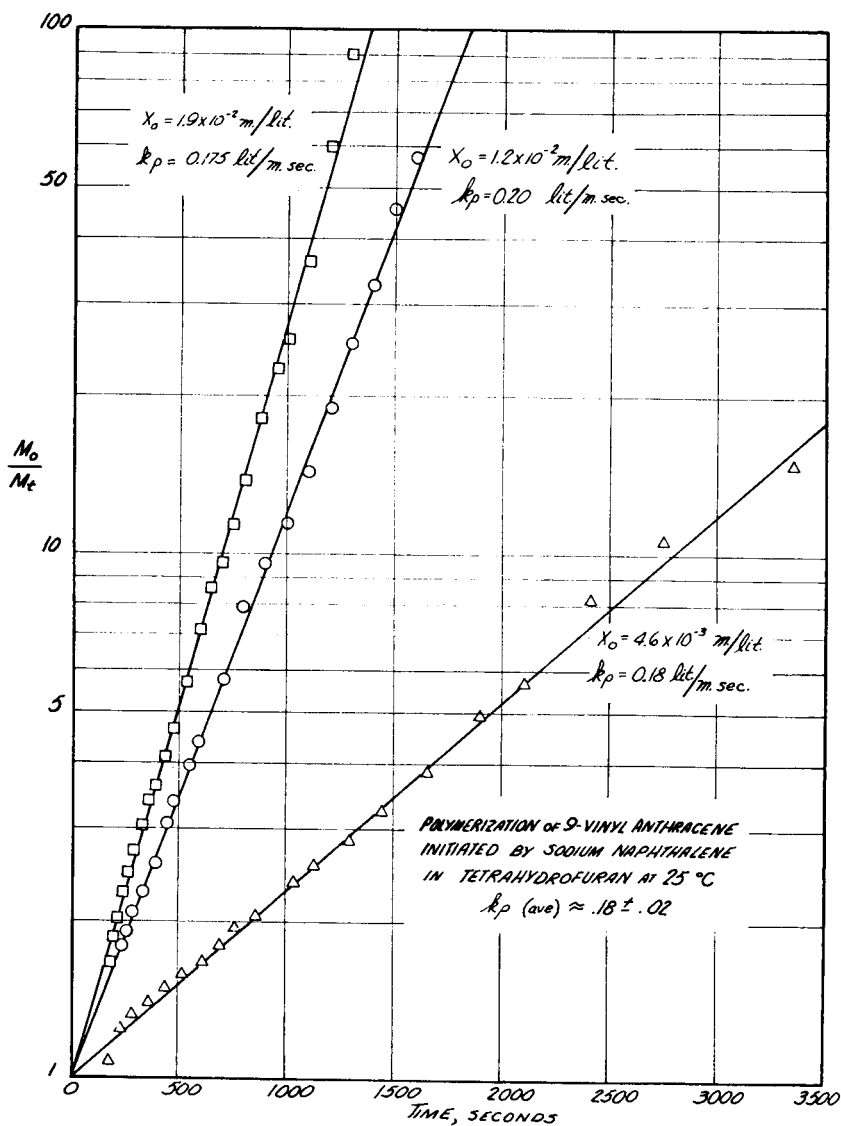


Fig. 1. The effect of initiator concentration.

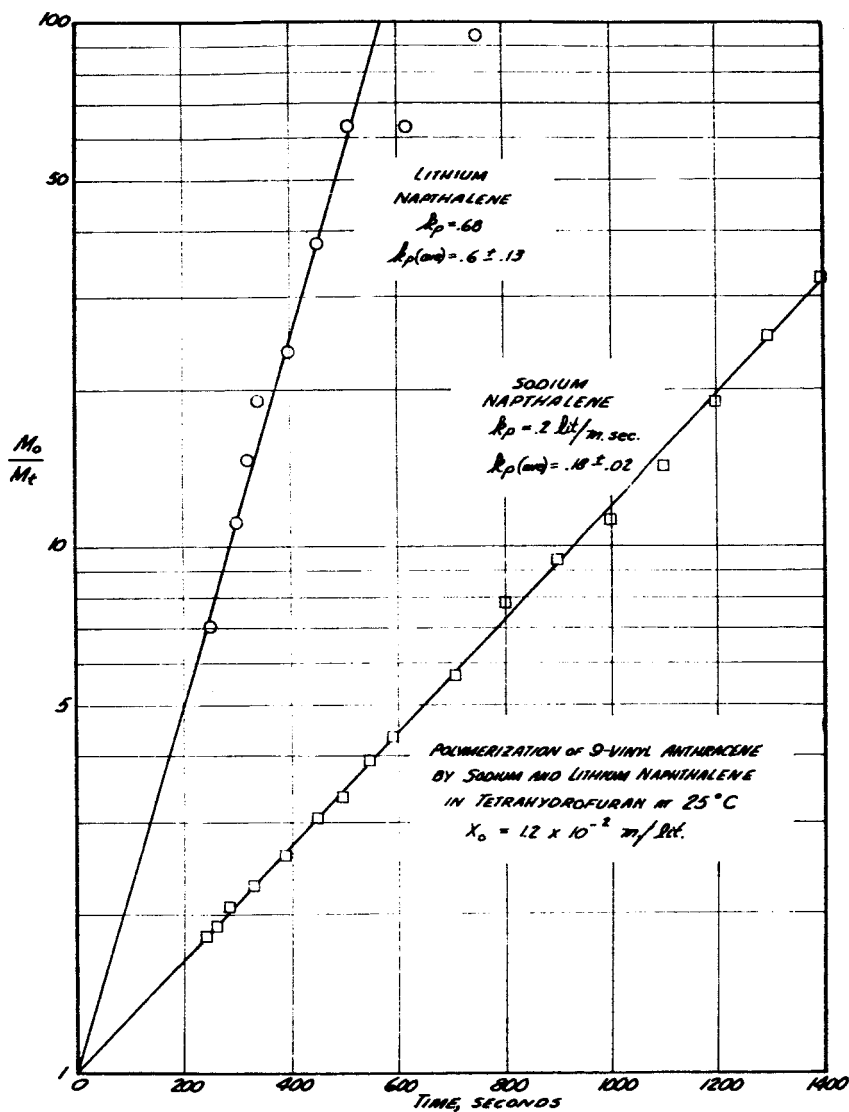


Fig. 2. The effect of cation.

thermore, additional experimental results show that the molecular weight does not change in the course of polymerization and also repeated additions of monomer to the "living" polymer increased the amount of polymer without affecting the molecular weight. These facts exclude chain transfer to polymer.

TABLE I
Anionic Polymerization of 9-Vinylnanthracene ^a at 25°C.

Initiator	X ₀ , moles l ⁻¹ × 10 ³	M ₀ , moles l ⁻¹ × 10 ³	K _p , l moles ⁻¹ sec. ⁻¹	P _n , degree of polymerization	Yield, ^b wt. %
Na naphthalene	1.0	12.3	0.20	7.6	90
"	0.75	3.2	0.30	7.3	71
"	0.81	19.0	0.17	8.2	83
"	0.69	31.0	0.27	7.9	80
"	0.51	4.6	0.18	-	60
Li naphthalene	0.72	24.0	0.45	6.9	84
"	0.71	12.0	0.68	8.4	85
"	1.20	35.0	0.55	11.9	70
"	0.44	2.1	0.41	8.4	-
"	0.67	1.4	0.55	9.6	88
"	0.81	1.4	0.94	9.9	91
Butyllithium ^c	0.83	55.0	-	5.8	99
"	0.83	42.0	-	5.9	78
"	1.0	210.0	-	8.4	50
"	0.40	16.0	-	8.9	85
Butyllithium ^d	0.40	20.0	-	6.7	87
"	0.40	40.0	-	5.4	95
"	0.40	100.0	-	4.5	96

^a Additional results showing the relative constancy of molecular weights as well as the unusual structure of the polymer have been published recently (1).

^b Based on material insoluble in methanol.

^c Kinetic runs at 50°C. in benzene without titration of impurities.

^d At 50°C. in THF.

To ascertain whether chain transfer to solvent is involved, several dilatometric runs with butyl lithium initiation in benzene were performed in the complete absence of THF (Table I). Owing to the simultaneous occurrence of initiation and propagation by a mechanism outlined by Bywater (4) and Morton (5), the absolute rate constant could not be determined here. However, the similarity of the degree of polymerization in two solvents of very different properties makes chain transfer to solvent appear very unlikely.

Chain transfer to impurities constitutes a remote possibility. Although a step of this type is compatible with the observed kinetics, its occurrence is highly improbable as the purity of the monomer was shown to be of the order of 99.5% (1). Normally over 10 mole % of impurity would be required to reduce the molecular weights to the low values found experimentally.

A change in the counterion from sodium to lithium (Table I) resulted only in an acceleration of the rate (shown in Fig. 2) without affecting the degree of polymerization appreciably. This confirms previous results on styrene (6). A preliminary study of the temperature effect indicates a very high activation energy of the propagation step (8-15 kcal./mole), but no change in the molecular weight.

In this connection, it is interesting to note that the fractionation of poly-9-vinylanthracene showed the material to be polydisperse (1) and also that the anionic polymerization of acenaphthylene obeys similar kinetics and yields low molecular weight polymers (7). These facts offer additional support to the postulated chain transfer step in the anionic polymerization of 9-vinylanthracene.

On the basis of the experimental results outlined here, we may conclude the following:

(1) The linearity of all the kinetic experiments in THF leaves little doubt that the concentration of active sites remains constant throughout the run and, therefore, chain termination by impurities cannot occur to any significant extent. It also indicates that the reaction obeys the previously (2) found relationship.

$$-(dM/dt) = k_p X M$$

where X is the initiator concentration and M the monomer concentration.

(2) The maximum degree of polymerization obtainable by an anionic mechanism is limited by a chain transfer reaction, most probably to monomer.

(3) The ratio of the chain transfer rate constant to the propagation rate constant is essentially independent of concentrations, nature of the solvent, counterion, and temperature.

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